Lab Report XRF 449

Analysis of solar cells using Micro-XRF

Solar cells are becoming increasingly popular for power generation. Their efficiency is determined mainly by their chemical composition and physical structure. The chemical composition is of particular interest for thin-film structures. In most cases the absorber of thin film cells is produced from CIGS-structures, which are Cu-In-Ga-Se or Cu-In-Ga-S compounds. Contact and passivation layers complete the structure of a thin-film cell.

For technology development and quality control during the manufacturing process it is important to check primarily composition but also thickness of these layers as well as their homogeneity. Due to lack of suitable reference samples the analysis has to be standardless. Nevertheless, it is possible to use EDS to verify analytical results.

Instrumentation

The analyses were performed with the Bruker instruments M1 MISTRAL and M4 TORNADO. Both instruments are Micro-XRF spectrometers but use different measurement conditions. The M1 MISTRAL can only measure in air and uses collimators which limit spot sizes to 300 µm. The M4 TORNADO can also measure in vacuum and produces spot sizes down to 25 µm using poly-capillary X-ray optics. The price for the increased resolution is the influence of the optics on the excitation spectrum, in particular a reduction of excitation intensity for high energies.

Both instruments use silicon drift detectors for detecting fluorescence radiation that offer high count rate capability combined with good energy resolution.

Sample structure

CIGS-solar cells are typically manufactured by deposition on glass substrates which are coated with a Mo-contact layer. The CIGS-absorber in turn is coated with a top contact layer and a passivation layer. These are often CdS and ZnO, respectively. Depending on the manufacturing process, it is possible to analyze the CIGS-composition with or without the top layers. Because the CdS-layer is very thin the sensitivity for the elements of this layer needs to be very high.

A typical layer structure is shown in Fig. 1.

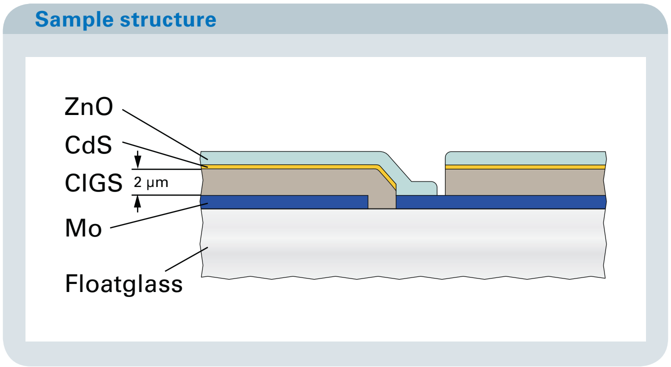

Fig. 1 Typical structure of a CIGS solar cell.

Table 1 Thickness and composition of sample layers

Layer data

Layer	Thickness/nm	Composition/wt.%
Mo	500–1,500	100
CIGS	1,000–3,000	Cu ~20, In ~20 Ga 5–10, Se ~50
CdS	20–50	Stoichiometric
ZnO	500–2,000	Stoichiometric

Comparison of measurements in air and in vacuum

The CIGS-layers were analyzed using different measurement conditions. At first the influence of the measurement medium (air, vacuum) was examined. This was done for the CIGS-layer only. Differences due to the absorption in air are only significant in the low energy range, as can be seen in Fig. 2.

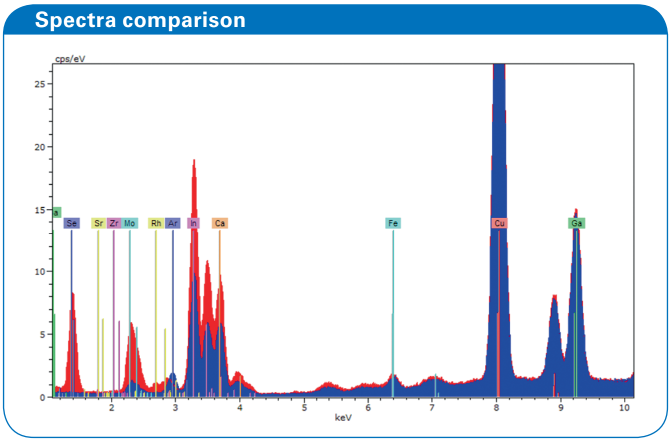

Fig. 2 Spectra of a CIGS-layer measured in air (blue) and vacuum (red).

The intensity for In-L-radiation measured in vacuum is better by a factor of 2 than for the measurement in air. All other element lines are either not strongly influenced by absorption (Cu, Ga) in air or not relevant for quantification (Si from glass).

Comparison of excitation with poly-capillary optics and with collimators

Solar cells are homogeneous. Therefore a position sensitive analysis is not required. On the other hand a non-destructive analysis of large samples is required, which is possible using Micro-XRF spectrometers, as they are equipped with a sample stage that can move the sample into different measurement positions. The excitation for small areas is possible with X-ray optics (poly-capillaries) or with collimators. The advantage of X-ray optics is the high excitation intensity. On the other hand the excitation spectrum is determined by the transmission function of the optics, which influences the measured spectrum. This can be seen in Fig. 3 for the measurement of a CdS-CIGS-structure using a Rh-tube with capillary optics and a W-tube with collimator (1 mm).

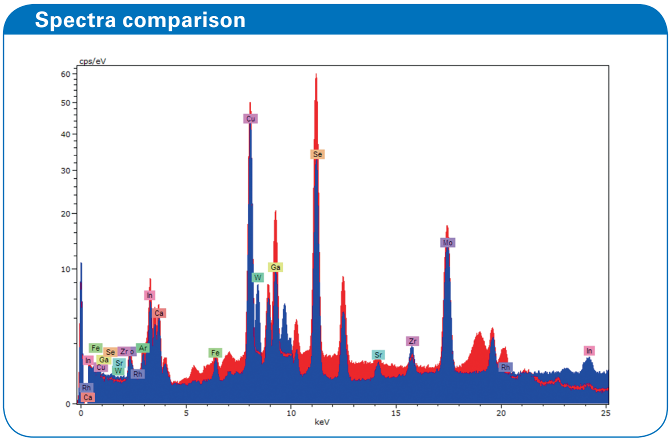

Fig. 3 Spectra of a CdS-CIGS-structure measured with Rh-tube and poly-cap optics (red) and with W-tube and collimator (blue) measured in air.

The spectra show very similar intensities for the elements Cu, Ga and Se. Significant differences can be seen for In from the CIGS-structure and for Cd from the CdS-layer. The high energy K-lines provide acceptable intensities only for excitation with the collimator. The lower energetic L-lines are better excited in both modes, but there are strong overlaps with each other as well as with Ca from the glass and Ar from the air. Nevertheless, these overlaps can be dealt with using peak deconvolution procedures.

The Cd and In intensities for the excitation with the poly-capillary optics are only slightly better. Therefore it will also be possible to use the collimator with a W-tube for excitation.

Quantification

Standardless models are required for the quantification of CIGS-structures because no references are available. Standardless quantification uses only pure element intensities of the layer constituents, but there is a possibility for cross checking quantification results by EDS in a scanning electron microscope. In that case the sample has to be cut and embedded in epoxy. Then the sample can be polished and the cross section can be analyzed both for thickness and for composition. If the XRF-examinations were performed before preparation comparisons between both methods are possible.

Analysis of a CIG-structure

At first a CIG-structure (after deposition of Cu, In and Ga) was examined. Fig. 4 shows the analysis results of a cross section of this structure in a SEM. The upper part is a backscattered electron image of the sample. From that cross section the thickness of the different layers can be measured directly. The green line indicates the position

Line scan

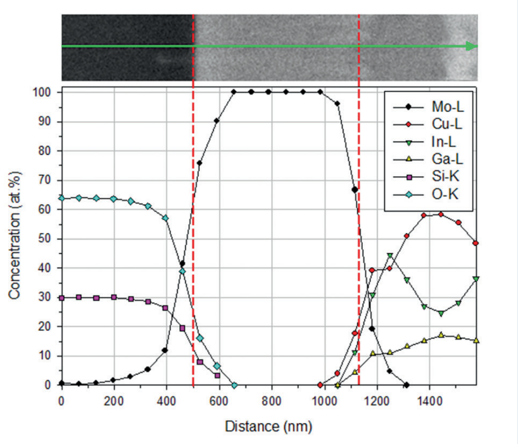

Fig. 4 Line scan over a CIG-structure

of the line scan. The lower part of the figure shows the distribution of element concentrations along this line. These measurements were performed at 25 positions with a total measurement time of 416 s.
In the cross section the sample can be considered as homogeneous. Here a standardless quantification with EDS is possible. These results can be compared with the standardless XRF-quantification. For XRF 3 repeated measurements with the M1 MISTRAL were performed with 40 kV, 800 µA for 60 s and a collimator size of 1.5 mm which results in a total measurement time of 180 s per sample. Results of both analytical methods are summarized in Table 2.

Table 2 Quantification results for a CIG-layer with statistical error

Quantification of CIG-layer

Method	Layer	n	Thickness /nm	Composition /wt.%		
				Cu	Ga	In
EDS	Mo	7	630			
XRF	Mo	3	509 ± 2			
EDS	CIG	10	620	33.8 ±7.3	7.0 +2.2	58.6 +8.0
XRF	CIG	3	583 ± 4	30.1 +0.3	8.1 +0.1	61.8 +0.2

The agreement of both methods is satisfactory. It can be seen that the statistical error of the EDS measurement is significantly larger, also if the measurement time is longer. This is caused by the inhomogeneity of the layer over its thickness. This inhomogeneity will not be detected with the XRF measurement perpendicular to the sample surface. The determination of thickness depends on the correct calibration of the SEM-magnification. Additionally it will be influenced by the evenness of the layer system and clearly defined intersections between the layers.

Analysis of a CIGS-Structure

Next a complete CIGS-structure was analyzed. Here both the comparison with EDS measurements and a cross check with WDXRF measurements [1] were performed. Results are shown in Table 3.

Table 3 Quantification results for a CIGS-layer with statistical error

Quantification of CIGS-layer

Method	Layer	Thickness /nm	Composition /wt.%			
			Cu	Ga	Se	In
EDS	Mo	952				
Micro-XRF	Mo	884				
WDXRF	Mo	900				
EDS	CIGS	1620	18.1	11.2	52.5	18.3
Micro-XRF	CIGS	1643	17.9	9.45	52.8	19.8
WDXRF	CIGS	1653	18.4	12.2	51.1	18.3

These results show a good agreement between all methods. The thicknesses for both XRF-methods are in excellent agreement. The thickness derived from the SEM-image deviates slightly. The compositions determined by all methods are in good agreement too. Because results of EDS depend on the lines used, it is necessary to mention that the results presented are calculated by using K-lines of Cu, Ga and Se. The accelerating voltage of the SEM was set to 20 kV.

Table 4 Repeated measurements on a CIGS-structure with mean values and relative standard deviations

Quantification of CIGS-structure

Parameter	d Mo /µm	d CIGS /µm	Cu /wt.%	Ga /wt.%	Se /wt.%	In /wt.%
1	0.478	1.149	17.71	6.29	46.12	29.87
2	0.477	1.174	17.66	6.18	45.07	31.09
3	0.475	1.157	17.87	6.50	45.91	29.72
4	0.473	1.158	17.79	6.26	45.50	30.44
5	0.476	1.154	17.99	6.26	45.66	30.09
6	0.463	1.144	17.76	6.25	45.23	30.76
7	0.468	1.129	17.71	6.39	46.02	29.88
8	0.469	1.155	17.50	6.06	45.29	31.15
9	0.469	1.143	17.82	6.41	45.42	30.35
10	0.465	1.137	17.92	6.27	45.38	30.43
11	0.472	1.162	17.79	6.14	45.40	30.66
12	0.476	1.166	17.63	6.31	45.60	30.46
13	0.477	1.184	17.67	6.16	44.32	31.85
14	0.474	1.161	17.82	6.21	46.05	29.92
15	0.470	1.157	17.91	6.18	45.89	30.02
16	0.474	1.143	17.83	6.36	45.84	29.98
17	0.475	1.162	17.99	6.41	45.43	30.17
18	0.480	1.154	17.65	6.25	46.06	30.04
19	0.475	1.165	17.72	6.16	45.59	30.53
20	0.471	1.153	17.82	6.20	45.65	30.33
21	0.474	1.137	17.77	6.22	46.03	29.98
22	0.470	1.141	17.88	6.48	46.11	29.52
23	0.467	1.136	18.16	6.24	46.09	29.51
24	0.467	1.154	17.79	6.20	45.95	30.05
25	0.469	1.145	17.91	6.43	45.79	29.87
Mean	0.472	1.153	17.80	6.27	45.66	30.27
s (%)	0.92	1.10	0.78	1.80	0.91	1.77

Repeatability of measurements

25 measurements were performed in the same position of the sample to test repeatability with the M1 MISTRAL. Measurement time was 60 s. The quantification results displayed in Table 4 show the high reproducibility of these measurements. The average results are summarized in the last two rows as mean value and as relative standard deviation s. The relative standard deviations are approx. 1 %. They are mainly determined by measurement statistics.

Examination of sample homogeneity

An examination regarding homogeneity of the CIGS–samples was performed by measurements in different locations over the sample. 5 repeated measurements were performed at a total of 4 positions. The results for the CIGS-layer are contained in Table 5.

Table 5 Results of homogeneity test with mean values and standard deviations

Homogeneity test

Parameter	d CIGS /µm	Cu /wt.%	Ga /wt.%	Se /wt.%	In /wt.%
Pos 1-1	1.111	17.92	9.56	46.69	25.83
Pos 1-2	1.115	18.45	9.48	45.96	26.11
Pos 1-3	1.123	18.01	9.48	45.8	26.72
Pos 1-4	1.113	17.92	9.46	46.23	26.39
Pos 1-5	1.114	18.13	9.58	46.76	25.53
Mean	1.115	18.086	9.512	46.288	26.116
s	0.005	0.221	0.054	0.428	0.465
Pos 2-1	1.144	17.87	9.35	46.44	26.34
Pos 2-2	1.124	18.06	9.71	46.2	26.03
Pos 2-3	1.134	18.39	9.65	46.46	25.5
Pos 2-4	1.133	18.29	9.65	46.69	25.38
Pos 2-5	1.13	18.25	9.36	46.48	25.91
Mean	1.133	18.172	9.544	46.454	25.832
s	0.007	0.207	0.174	0.174	0.393
Pos 3-1	1.095	17.94	9.62	46.88	25.56
Pos 3-2	1.096	18.01	9.49	46.4	26.1
Pos 3-3	1.1	17.99	9.46	46.26	26.28
Pos 3-4	1.09	18.39	9.59	46.75	25.28
Pos 3-5	1.096	18.09	9.62	46.63	25.67
Mean	1.095	18.084	9.556	46.584	25.778
s	0.004	0.179	0.076	0.253	0.407
Pos 4-1	1.1	18.16	9.74	46.97	25.14
Pos 4-2	1.119	18.08	9.28	46.18	26.46
Pos 4-3	1.118	18.12	9.32	46.34	26.22
Pos 4-4	1.124	18.06	9.54	46.19	26.2
Pos 4-5	1.128	17.97	9.33	45.83	26.87
Mean	1.118	18.078	9.442	46.302	26.178
s	0.011	0.072	0.195	0.418	0.640

The examination shows that the sample is homogeneous. The variation of thickness and composition of the CIGS-layer at different locations is small. This conclusion is supported by the summary of measurements in Table 6.

Table 6 Summary of homogeneity measurements

Summary of homogeneity test

Parameter	d2 /µm	Cu /wt.%	Ga /wt.%	Se /wt.%	In /wt.%
Mean	1.115	18.105	9.514	46.407	25.976
Mean of s	0.007	0.170	0.125	0.318	0.476
s of mean	0.015	0.045	0.051	0.140	0.200

These data show that the standard deviations of the mean values of measurements at every point (second data row) are even larger than the standard deviation of the mean values itself. That means that the fluctuations of quantification results in one spot due statistics are larger than the fluctuations of the mean values for different spots.

Summary

The analysis of thin film solar cells can be successfully performed with Micro-XRF. It is possible to measure the structures both in air and in vacuum. The absorption in air for the lowest energies is not too high. Thus this method can be comfortably used for in-line control during the production process as well as for final testing.
Quantification can be done only standardless due to the lack of references. Comparisons with EDS and with WDXRF show good agreements regarding the composition of layers. For EDS quantification results depend on the element lines used.
For all these methods the results for layer thickness are in very good agreement.

References

[1] These samples were manufactured and measured with WD-XRF by R. Caballero at Helmholtz-Zentrum Berlin

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